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Determination of nickel, copper, zinc and lead in human scalp hair in Syrian occupationally exposed workers by total reflection X-ray fluorescence

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Abstract The concentrations of Ni, Cu, Zn, and Pb in human scalp hair of 281 individuals working in 10 Syrian industrial plants were determined using co-precipitation by ammoniumpyrolidinedithiocarbamate (APDC) method for total reflection X-ray fluorescence (TXRF) analysis. The results were compared to data obtained for a control group consisted of individuals working at the Syrian Atomic Energy Commission and also to data reported in the literature. The results given by the group of workers in battery plant showed that Pb concentration in human scalp hair samples were higher than those for control group, while some abnormal concentrations were obtained for Cu, Zn and Ni in cables, printing and battery plants, respectively. Normal concentrations of these elements were obtained for hair workers in olive oil, power stations, textile, and iron industrial plants. The relationships of Pb–Pb/Ni and Cu–Cu/Ni were plotted with correlation coefficients of 0.9937 and 0.9014, respectively. In general, the results showed that, the workers who were occupationally exposed to battery industrial pollution are at risk, followed by individuals in printing and cables industries, while the rest of workers in other industries are considered occupationally unexposed.

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Keywords Industrial plants · Occupational exposure · Scalp hair · Total reflection X-ray fluorescence · Trace elements

Introduction

During the past three decades the investigation of trace element concentrations in human scalp hair has become increasingly popular for monitoring environmental exposure (Dede et al. 2001; Faghihian and Rahbarnia 2002; Rauf and Jervis 1992), evaluating systematic intoxication (Katz and Katz 1992; Oliveira-Santos et al. 2002), assessing nutritional status (Dede et al. 2001), and diagnosing diseases (Raghavaiah et al. 1996). Studies showed that scalp hair can record the level and changes of many elements in the body over a long period of time (Saiki et al. 1998). Changes in the elemental composition of hair are believed to depend on alterations of external and internal media of the human body, and it is considered that the hair of healthy individuals contains each element within a well defined range of concentration (Kolmogorov et al. 2000; Man et al. 1996), and it can be considered as a potential indicator of both external and internal long-term exposure to environmental pollutants.

The idea of hair analysis is very inviting, because it is easily painlessly removed, normally discarded,

easily collected, transported and stored and it contains relatively high concentrations of different minerals and trace elements. Various different techniques such as neutron activation analysis (NAA; Abugassa et al. 1999; Faghihian and Rahbarnia 2002; Lin and Henkelmann 2003; Menezes et al. 2004), atomic absorption spectrometry (AAS; Sturaro et al. 1993), and atomic emission spectrometry (AES; Asfaw and Wibetoe 2004; Matusiewicz and Kopras 2003) have been employed in the detection of trace metals presented in human hair. X-ray fluorescence (XRF) spectrometry is also applied to hair analysis (Dede et al. 2001; Kolmogorov et al. 2000), although the determination of some trace elements, such Pb, Ni, Mn, and Cr, produces particular difficulties. Total reflection X-ray fluorescence (TXRF) is a special method of XRF analysis. During the last decades, TXRF has been adopted as an established technique for multi-element determination of trace elements in various type of matrixes (Martinez et al. 2004). Recently, we have optimized the co-precipitation method using APDC reagent for TXRF analysis of some metals with low level of concentration (Khuder et al. 2007). The optimized TXRF method was applied for the determination of Ni, Cu, Zn, and Pb in whole blood as well as in human hair of non-occupationally exposed Syrian individuals.

The present study was aimed to determine Ni, Cu, Zn, and Pb elements in scalp hair of occupationally exposed individuals using an optimized TXRF. The results should reflect the occupational situation of workers in different industrial plants in the country. This study was also set out to gather information on the effects of some factors, such as duration of work, type of occupation and smoking habit, on element levels in scalp hair of studied groups. Also, the correlation between each pair of elements will be investigated.

Experimental

Population tested

During 2005–2006, Ni, Cu, Zn, and Pb were measured in human scalp hair of 281 individuals, working in different industrial plants in Syria. The workers in these plants were between 21–59 years old. The industries were chosen in a manner that reflected releases of specific elements into environment, e.g. Pb and Ni expected to be released from battery plants, Cu from cables factories, and Zn from printing plants. Other industries as newspaper printing, power stations, olive oil, and textile plants, which expected to show relatively a small or a negligible impact of elemental pollution, were chosen to study the concentration range of metals and to compare between the occupational situations of workers in different industrial plants in the country. However, the chosen industries were: two printing plants (P1,P2), one olive oil plant (P3), one cables factory (P4), two power stations (P5, P6), one public newspaper (P7), one batteries production plant (P8), one textile company (P9), and one iron factory (P10). Plants are located in different provinces in the country: P1 (n=32), P2 (n=26), P3 (n=20), P4 (n=28), P6 (n=20), P7 (n=22), and P9 (n=21) plants are in Damascus city in south of Syria. P5 (n=8) and P10 (n=50) plants are in Hama City in the middle of Syria. Finally, P8 plant (n=54) is in Allepo City in the north of Syria. All workers were given a questionnaire designed to obtain information on some factors that known to have some impacts on element contamination, e.g. duration of work which is divided to some subcategories listed in Table 1 and smoking factor that may affect the Pb hair levels. According to chosen groups, about 54% of the workers in the studied

Table 1 Distribution of duration of employment in the studied plants and at SAEC (control group)

Duration (years)	Group of workers examined											
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	Total	C
<5	8	2	7	0	0	2	3	4	0	0	26	22
5–10	16	16	9	4	2	6	5	12	5	5	80	13
11–20	7	5	4	4	6	10	6	26	10	16	94	8
>20	1	3	0	20	0	2	8	12	6	29	81	5
Total	32	26	20	28	8	20	22	54	21	50	281	48

P1 and P2 are the two printing plants; P3 is the olive oil plant; P4 is the cable factory; P5 and P6 are the two power stations; P7 is the public newspaper; P8 is the battery plant; P9 is the textile plant; P10 is the iron factory; C is the control group.

plants were smokers. Number of smokers in each plant is reported in Table 2. In this study, the elemental levels could vary, depending upon the nature of occupation, where some occupations as smelting and braiding in battery and cables industries, respectively, were expected to have an intensive impact on metals contamination, in contrast to other working environments such as administrative works. Questionnaires were also given to workers in a control group, which consisted of forty-eight individuals working in different departments at Syrian Atomic Energy Commission.

Hair samples from 281 workers in the previously mentioned plants and from 48 unexposed workers, who consisting the control group, were collected to check for the presence of Ni, Cu, Zn, and Pb in hair. Hair samples were selected from different points of the head and subjected to the surface cleaning treatment according to IAEA recommendation (Kolmogorov et al. 2000), fragmented and kept in polyethylene bottles for further analysis.

Sample preparation

For the digestion of human hair samples, a mixture of HNO_3–H_2O_2 with a ratio of 3:1 was used. A volume of 1 ml of this mixture was added to each human hair sample (the mass of each sample was 0.100 g) in 10 ml glass tubes. The temperature was gradually increased and finally maintained at 150°C for 30 min.

Table 2 Number of smokers and nonsmokers in the studied plants

Group of workers examined	Number of non-smokers	Number of smokers	Total
P1	15	17	32
P2	23	3	26
P3	10	10	20
P4	10	18	28
P5	1	7	8
P6	10	10	20
P7	8	14	22
P8	15	39	54
P9	12	9	21
P10	25	25	50
Total	129	152	281

See Table 1 for definitions of groups

Table 3 Mean levels, medians, range of concentrations, and confidence intervals at 95% for trace elements (ppm) in scalp hair from workers employed in different industrial plants in Syria and from workers employed at the Syrian Atomic Energy Commission (control group)

Group	Ni	Cu	Zn	Pb
P1	2.74±0.72[a]	8.94±2.95	184±116	2.51±1.73
	2.58[b]	8.45	164	1.88
	1.61–4.33[c]	4.79–13.8	71.3–717	0.90–7.16
	1.33–4.15[d]	3.16–14.7	0–411	0.88–5.90
P2	2.97±1.69	10.1±9.38	289±299	8.46±4.99
	2.31	6.88	173	7.00
	1.74–8.81	1.19–44.2	75.9–1520	2.32–18.9
	0–6.28	0–28.5	0–875	0–18.2
P3	1.55±0.56	5.03±2.17	141±64.9	1.95±2.54
	1.45	4.55	134	1.22
	0.75–3.04	2.39–11.2	41.7–322	0.42–12.2
	0.45–2.65	0.78–9.28	14–268	0–6.93
P4	1.63±0.56	26.1±26.0	124±56.7	4.39±5.54
	1.56	17.8	117	2.05
	0.76–3.07	2.3–109	31.5–241	0.68–26.0
	0.53–2.73	0–77.1	13–235	0–15.3
P5	2.23±1.24	8.00±6.68	136±47.9	2.17±1.28
	1.83	5.90	118	1.79
	1.33–5.09	4.0–24.3	88.7–229	0.77–4.14
	0–4.66	0–21.1	42.1–230	0–4.68
P6	2.63±1.19	9.13±1.71	166±48.3	4.97±3.33
	2.37	9.10	177	4.58
	1.64–6.43	5.7–12.1	64.4–235	0.96–11.8
	0.30–4.96	5.78–12.5	71.6–260	0–11.5
P7	1.94±0.63	8.36±3.63	157±52.2	4.93±6.15
	1.80	7.25	153	2.35
	1.10–4.17	3.6–19.7	86.2–279.1	1.11–24.7
	0.70–3.18	1.24–15.5	55.0–259	0–17.0
P8	4.53±2.96	9.31±4.51	158±62.8	408±629
	3.66	8.41	150	198
	2.06–15.5	3.3–24.7	59.8–328	18.8–3625
	1.27–10.3	0.47–18.2	35.0–281	0–1641
P9	1.89±0.46	5.74±2.56	103±31.7	2.20±1.92
	1.87	5.59	103	1.43
	1.20–2.83	2.72–10.5	42.1–156	0.54–8.00
	0.99–2.79	0.72–10.8	40.9–165.1	0–5.96
P10	1.97±0.79	6.48±3.50	135±57.8	2.42±2.99
	1.89	6.00	129	1.60
	0.65–4.76	0.78–17.8	45.5–298	0.45–19.5
	0.42–3.52	0–13.3	22.0–248	0–8.28
C	2.58±1.19	15.6±5.7	260±113	10.7±8.9
	2.31	14.2	235	6.80
	1.06–5.95	6.20–40.6	109–759	1.60–37.4
	0.25–4.91	4.40–26.8	38–482	0–28.1

See Table 1 for definitions of groups.

[a] Mean ± SD

[b] Median

[c] Concentration range

[d] Confidence interval at 95%

Table 4 Normal concentrations and ranges of trace elements in human hair published in the literatures (in ppm)

Reference	Ni	Cu	Zn	Pb
Faghihian and Rahbarnia 2002	nd	4.6–66.7	36–329	nd
Dede et al. 2001	nd	9.12–29.3	68.9–456	nd
Sturaro et al. 1993	1.4–3.2	10–21	171–314	6.5–8.7
Carvalho et al. 1998	1.1–4.3	9–83	110–1092	3.3–99.1
Eltayeb and Van-Grieken 1989	nd	7–22	89–170	3–17

nd Non-determined

The digestion solutions were evaporated to dryness; each residue was dissolved with sub-boiled concentrated HNO_3, then the obtained solutions were taken up with 1.0 ml. Trace metals in human scalp hair samples were then precipitated by APDC solution as follows: a volume of 2 ml of 1% APDC was added to each sample solution, which was adjusted to pH 3.5. Each solution was thoroughly mixed and settled for 30 min. The obtained metal–APDC precipitates were filtered using 0.45 μm pore size filter paper. To fulfill the requirement of TXRF analysis, each precipitate was dissolved by 1 ml of concentrated HNO_3. Then, 10 μl of 1,000 $\mu g.ml^{-1}$ Ga-standard solution was added to each solution, thoroughly mixed, and finally 10 μl of each obtained solution were pipetted onto sample carrier and evaporated to dryness.

Apparatus

The TXRF Spectrometer ISO 2000 (Italstructures Co.) with molybdenum excitation has been used. The spectrometer was equipped with Si(Li) detector (30 mm^2 active area and a resolution of 180 eV at 5.9 keV) and 2 kW x-ray tube (fine-focus 8×0.4 mm^2, Be window 400 μm) operating at 30 mA and 45 kV.

Reagents

Analytical grade acetone (Merck) and distilled water were used for washing human hair samples; 14 N HNO_3 pure for analysis (BDH) and 30% H_2O_2 (Fluka) were used for digestion of human hair samples; ammoniumpyrolidinedithiocarbamate (APDC) analytical grade (Merck) was used for the co-precipitation of trace elements. Gallium element standard, 1,000 μg/ml (BDH) served for internal standardization by TXRF.

Results and discussion

Analysis of hair samples

The human scalp hair samples were collected from 281 persons, working in 10 different industrial plants in the country. The samples were collected during a routine medical monitoring of the human health

Table 5 Comparison of hair trace element levels in individuals working in different Syrian industrial plants with those in the control group

Industrial plant	Ni			Cu			Zn			Pb		
	D[a]	CI[b]	E[c]	D	CI	E	D	CI	E	D	CI	E
P1	0	32	0	0	32	0	0	31	1	0	32	0
P2	0	23	3	4	21	1	0	23	3	0	26	0
P3	0	20	0	9	11	0	0	20	0	0	20	0
P4	0	28	0	0	15	13	1	27	0	0	28	0
P5	0	7	1	1	7	0	0	8	0	0	8	0
P6	0	18	2	0	20	0	0	20	0	0	20	0
P7	0	22	0	2	20	0	0	22	0	0	22	0
P8	0	48	6	4	50	0	0	54	0	0	5	49
P9	0	21	0	8	13	0	0	21	0	0	21	0
P10	0	50	0	15	35	0	0	50	0	0	50	0
Total No.	0	269	12	43	224	14	1	276	4	0	232	49

[a] Number of depleted results

[b] Number of results in the 95% confidence interval

[c] Number of elevated results

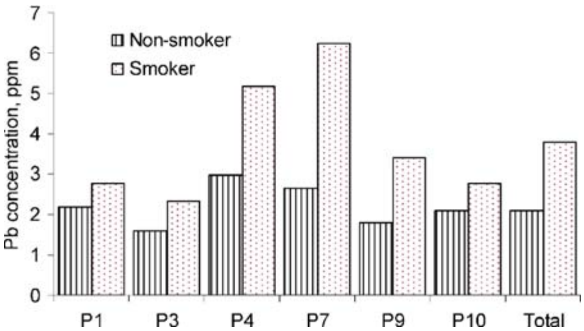


Fig. 1 Comparison between Pb levels in scalp hair of smokers and nonsmokers in different plants. Number of smokers and nonsmokers in each plant is shown in Table 2. Total numbers of nonsmokers and smokers in plants, corresponding to this study, are 80 and 92, respectively

attended by the Ministry of Health. Different metals, Ni, Cu, Zn, and Pb, in hair samples were determined using co-precipitation method of metals by APDC for TXRF analysis. In the term of detection limits, accuracy, and precision, the APDC–TXRF method was discussed in recently published work (Khuder et al. 2007). However, the method was applied for the determination of the previously mentioned elements with low concentrations in human hair samples. The results of analysis, including means, concentration ranges, median for each element, and confidence intervals at 95 % are shown in Table 3.

Nickel

Literature data (Table 4) showed that, the hair of healthy individuals contains Ni within a well defined range of concentration (Carvalho et al. 1998; Sturaro et al. 1993). In comparison to literature data, a normal distribution of Ni in scalp hair of individuals working in P1, P3, P5, P7, P9 and P10 Syrian industrial plants was obtained. Some abnormal Ni concentrations were obtained for workers in P2, P6, and P8 plants. The mean concentration of Ni in P8 plant was 1.8 times more than values reported for Syrian control group. The results in Table 5 show that six individuals (11.1% of the total number) working in battery plant have Ni elevated levels, confirming the presence of Ni contamination source in this industry.

Copper

Mean values of Cu in 10 industrial plants were ranged from 5.03 to 26.1 ppm. These values were comparable to those reported for different countries (Table 4). With one exception obtained for workers in cables factory, Cu in hair was normally distributed. Some individuals working in braiding division in cables factory have abnormal Cu concentrations, which were reached to 109 ppm. The results in Table 5 show that 13 workers (46.4% of the total number) in the previously mentioned industry have Cu elevated levels, indicating a contamination problem faced numbers of individuals working in cables factory. The number of depleted results for the workers in 10 plants was equal to 43 (15.3% of the total number). The low level of essential bio-elements as Cu in the individual's body may indicate the deficiency diseases, metabolic disturbances and physiological disorders (Dede et al. 2001).

Fig. 2 Pb levels in scalp hair of workers in different plants versus the duration of work. Definitions of groups and numbers of workers versus the duration of work are shown in Table 1

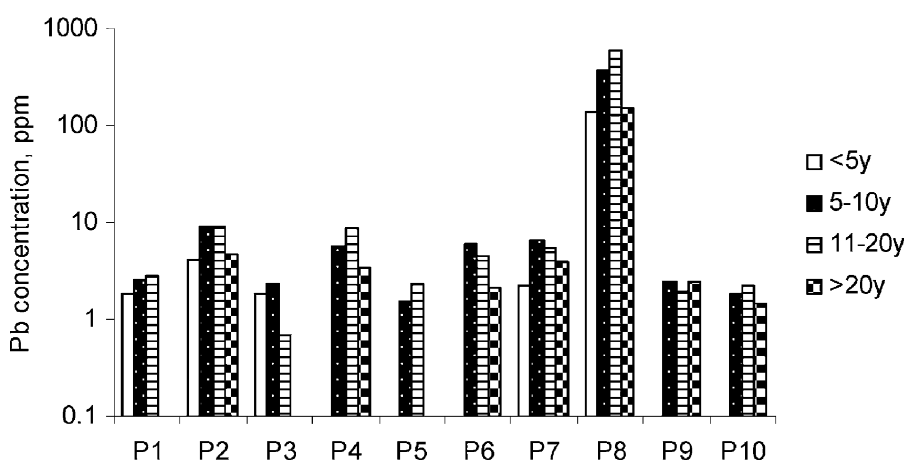
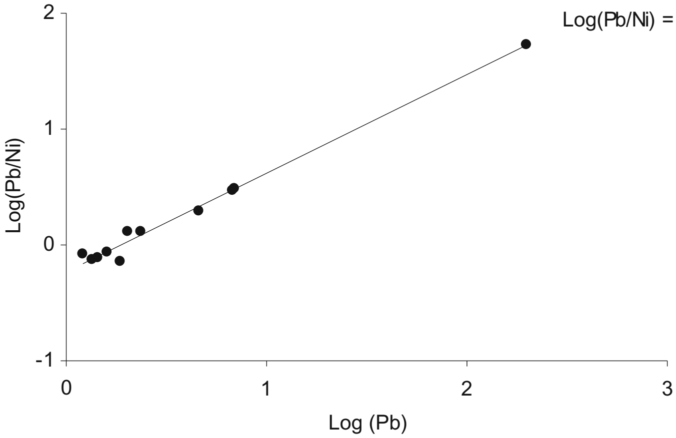


Fig. 3 Correlation between log (Pb) and log (Pb/Ni)



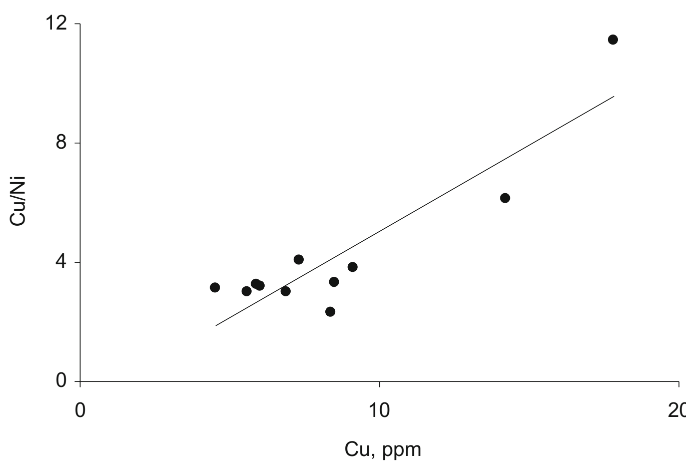
Zinc

A wide range of Zn concentration in scalp hair of unexposed population in different countries was reported (Table 4). In the present work, Zn concentrations in industrial plants from P3 to P10 were well agreed with those obtained for the Syrian control group and those reported for population in Iran, Turkey, and Italy (Dede et al. 2001; Faghihian and Rahbarnia 2002; Sturaro et al. 1993). While, some values for Zn concentrations were expanded to 717 and to 1,520 ppm in P1 and P2 plants, respectively. Results in Table 5 show that only three individuals (11.5% of the total number) working in P2 printing plant have Zn elevated levels.

Lead

Mean concentrations of Pb in scalp hair of workers in the studied plants were comparable to those obtained for control group (Table 3) and those reported in literatures (Table 4), with one exception obtained for workers in battery plant; whereas Pb means in scalp hair of workers in the last mentioned plant were 24.1, 39.2, and 62.3 times more than those values reported for Canadian individuals living in urban, New Zealanders living in different cities (City survey) and adults of USA, respectively (Fergusson 1990). The wide range of Pb concentration, 18.8–3,625 ppm, in scalp hair of workers in battery plant was compared to the range obtained elsewhere, e.g. the range of 70–3,700 ppm, which was reported for a group of Sudanese workers occupationally exposed to lead (Eltayeb and Van-Grieken 1989) and the range of 124–1,381 ppm, which was reported for lead workers of New Zealand population (Fergusson 1990). Furthermore, the trace element levels of the workers in battery plant were compared with the confidence interval of Pb obtained for control group (Table 3), taking into account that the confidence intervals for Pb and rest of elements were calculated from 95% *t*

Fig. 4 Correlation between Cu medians and Cu/Ni ratio



values. The results in Table 5 show that 49 individuals from 54 working in battery plant have Pb elevated levels, confirming a high percentage, 90.7%, of the total number of workers who exposed to high levels of Pb. Lead contamination sources may be existed by exhaust gases, metal dusts, some chemical used in the Battery plant. Study on an occupation factor showed that a mean concentration of Pb for 11 individuals working in smelting section in the Battery plant was equal to a value of 535 ppm, while for 10 individuals working in administration section in the same plant was equal to a value of 83.9 ppm.

The effect of smoking on mean concentrations of Pb in scalp hair of smokers in different plants was evaluated. Figure 1 shows that Pb means for scalp hair of smokers in plants of P1, P3, P4, P7, P9, and P10 were higher than these for nonsmokers by 1.26–2.34 times. In addition, Pb means for scalp hair of the total number of smokers (N=92) were also higher than these of nonsmokers (N=80) in the previously mentioned plants. Due to a small number of smokers and nonsmokers in P2 and P5 plants, respectively, Pb means were not shown in Fig. 1; while, due to the negligible effect of smoking versus the occupational factor, Pb means for smokers in P6 and P8 plants were not shown also.

Figure 2 shows that, Pb means were clearly increased by increasing duration of work from 5 to 20 years for workers in P8, while an inverse result was obtained for workers, having duration more than 20 years in the same plant. Similar results were obtained for individuals working in printing plants (P1 and P2).

Correlation between elements

In addition to arithmetic means which describe the central tendency of a set of results, Table 3 contains also medians which can be used when the asymmetrical distributions are dominated (Miller and Miller 1993). Median values were used in the correlation between concentrations of each pair of elements. Generally, the correlation between concentrations of each pair is appreciable when the intercept is near zero and the slope is higher than 0.5 (Faghihian and Rahbarnia 2002). In this work, the previously mentioned conditions were obtained only for two instances, relating the medians with the ratio of pair elements. In the first instance, a very good correlation coefficient, r, was obtained by plotting the relation between Pb medians and the ratio of Pb to Ni medians with a value equals to 0.9937. Figure 3 demonstrates the previously mentioned relationship as a function between log (Pb) and log (Pb/Ni), taking into accounts the wide range of Pb concentrations. In the second instance, r=0.9014 was obtained by plotting the relationship between Cu medians and Cu/Ni ratio (Fig. 4). Poor relationships were obtained for remaining instances.

Conclusions

It should be concluded that, the co-precipitation of trace elements: Ni, Cu, Zn, and Pb in scalp hair by APDC method for TXRF analysis was a suitable approach to reflect the occupational situation of workers in different industrial plants in the country. However, results showed that more than 90% of the workers in battery plant were exposed to high Pb levels, which mainly resulted by an occupational factor and a long-exposure period of time (5–20 years), but not due to additional factors as the smoking. In addition, different workers in battery plant, consisting 11.1% of the total number, had also Ni elevated levels. These results confirmed the lack to live in a healthier environment, which should include the improvement of working conditions and safety precautions in battery plant.

As a result of an intensive use of copper in cables industrial plant, Cu concentration levels in hair samples were higher than those for control group. The decrease of Cu concentration levels in hair of several workers in the studied plants may be related to a nutrition status. The normal distribution of Zn in most scalp hair samples was obtained, in exception of some anomalies obtained for workers in printing plants.

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